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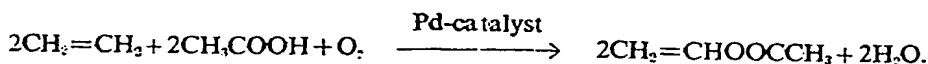


(54) PROCESS FOR THE MANUFACTURE OF VINYL ACETATE

(71) We, KNAPSACK AKTIENGESSELLSCHAFT, a body corporate organised under the Laws of Germany, of 5033 Knapsack bei Köln, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:

It is known that vinyl acetate can be produced in the gas phase from ethylene, acetic acid and molecular oxygen in accordance with the general equation:

15



For the catalyst, it is very important to have a fairly high activity so as to enable fairly small proportions of costly palladium to be used. In this case, it is possible for the reactor volume to be decreased at the same rate as the catalyst activity increases with the result that the operational costs are further reduced. Various processes have been described wherein the palladium catalyst is suggested to be used in combination with special addends in an attempt to increase its activity and obtain a commercially attractive process. The activators suggested to be used include, for example, the carboxylates and more particularly the acetates of lithium, sodium, potassium, rubidium, cesium, or of the alkaline earth metals (e.g. magnesium, calcium). Further useful activators are the metals copper, gold, zinc, cadmium, tin, lead, manganese, chromium, molybdenum, tungsten, uranium, iron, cobalt, nickel, niobium, vanadium or tantalum. The useful carriers include silicic acid, kieselguhr, silica gel, diatomaceous earth, aluminum oxide, aluminum silicate, aluminum phosphate, pumice, silicon

carbide, spinels, asbestos or active carbon.

Conventional vinyl acetate production processes are generally carried out by flowing a feed gas mixture of ethylene, acetic acid and oxygen over the catalyst, at elevated temperature and pressure. The catalyst which is in the form of lumpy or particulate material or similar material offering no great flow resistance to the gas travelling therethrough, may be placed in a tube that may be cooled for dissipating the heat of reaction.

The gas leaving the reactor can be cooled under pressure to eliminate condensable fractions consisting of the vinyl acetate produced, unreacted acetic acid and water. For the condensation of the reaction products, it is more economic to operate at elevated pressure than to use costly cooling media and operate at fairly low temperatures. The condensate is worked up by conventional distillation methods, residual reaction gas being recycled to the reactor, after replacement of the ethylene, acetic acid and oxygen consumed and, optionally, after separation of carbon dioxide. The vinyl acetate pro-

duced is contained in the crude matter obtained in the condensation step.

For the crude condensates it is highly desirable to contain a fairly high portion of vinyl acetate — this corresponds to a high acetic acid conversion rate — so as to permit economic work-up.

It has now unexpectedly been found that high vinyl acetate concentrations in the crude condensate or high acetic acid conversion rates coupled with an increased catalytic activity, expressed in grams vinyl acetate per liter of catalyst per hour, can be produced, using a particulate carrier material consisting of small particles with a diameter varying within certain limits.

The effect described above is already clearly observed in the case of particulate carrier material having a diameter of about 1.5 mm or less. The use of particulate carrier material with a size between 0.1 and 0.5 mm in a fluidized bed has more particularly been found to unexpectedly increase the catalytic activity, vinyl acetate concentration in the crude condensates, and acetic acid conversion rate. The crude condensate has, for example, been found to contain vinyl acetate in a concentration of about 45 weight percent, for a catalyst activity of about 1000 grams vinyl acetate per liter of catalyst per hour. It is interesting to state here that particularly the dissipation of the reaction heat can be readily achieved at the high catalytic activity in the fluidized bed.

The present invention relates more particularly to a process for the manufacture of vinyl acetate by reacting ethylene, acetic acid and molecular oxygen in the gas phase, if desired in the presence of one or more inert gases, at temperatures between 100 and 250°C, preferably between 150 and 220°C, under a pressure between 1 and 21 atmospheres absolute, preferably between 5 and 11 atmospheres absolute, and in contact with a carrier catalyst consisting of metallic palladium, a carrier and optionally one or more activators, which comprises carrying out the reaction in contact with a carrier catalyst of which at least 80% of the carrier particles have a diameter between 0.1 and 1.5 mm, preferably between 0.1 and 0.5 mm. The carrier preferably is silicic acid (SiO_2) and more preferably is globular or ball-shaped SiO_2 .

It is especially advantageous for the reaction to be carried out in contact with a fluidized bed carrier catalyst of which the carrier material is silicic acid (SiO_2) of which the individual particles have a diameter between about 0.1 and 1.5 mm, preferably between 0.1 and 0.5 mm.

It is also possible for the further carrier materials first mentioned above to be used

in the process of the present invention. The same is true of the activators recited hereinabove. To preserve the activity of the catalyst, it is also possible for the gas mixture travelling over the carrier catalyst to be used in combination with one or more alkali metal acetates or alkali metal compounds, which form alkali metal acetates under the reaction conditions and are added in quantities sufficient to replace the loss of alkali metal acetates occasioned by vaporization of the hot carrier catalyst.

Still further, it is possible for the chemically pure acetic acid to be replaced with less expensive formic acid-containing acetic acid, as the formic acid is subject to an almost quantitative decomposition over the carrier catalyst with the resultant formation of carbon dioxide and hydrogen which, however, undergoes immediate combustion with the oxygen.

EXAMPLE 1: (Comparative Example)

1 kg (= 1.85 liter) of a globular or ball-shaped silicic acid carrier (globules or balls = 2-2.5 mm in diameter) was mixed and thoroughly impregnated with a solution containing 11 grams noble metal ions, namely 8 grams Pd^{++} in the form of PdCl_2 and 3 grams Au^{+++} in the form of $\text{H}(\text{AuCl}_4)$. The resulting mixture was dried with agitation so as to uniformly distribute the noble metal salts on the carrier. The dry mass was introduced at 40°C into a 5 % aqueous hydrazine hydrate solution rendered alkaline by means of NaOH or KOH . Following the complete reduction of the noble metal compounds to the corresponding noble metals, supernatant liquid was poured off, the whole was thoroughly washed using distilled water, and the mass was impregnated, while still moist, with a 15 % aqueous potassium acetate solution. The solution was decanted and the impregnated matter was dried under vacuum at 60°C. The catalyst so treated was ready for use and contained, per liter, 5.95 grams noble metals or about 0.7 weight percent Pd , 0.26 weight percent Au and 4 weight percent K , in the form of CH_3COOK .

1.2 normal cubic meter/hr (measured at N.T.P.) feed gas composed of 61.5 % by volume C_2H_4 , 20.2 % by volume CH_3COOH , 7.1 % by volume O_2 and 11.2 % by volume CO_2 was passed through a catalyst furnace 2.8 meters long, which formed part of a commercial cycle system and contained 2 liters catalyst having the composition indicated above (solid bed catalyst). The feed gas entered the catalyst furnace at a pressure of 8 atmospheres absolute and the reaction temperature was 195°C. The contact time was 6.0 seconds, the gas load was 2.8 normal cubic meters feed gas mixture per liter of

catalyst per hour, and the velocity of flow was 48 cm/second. The reaction products were removed from the reaction gas by condensation, unreacted acetic acid was distilled off and recycled to the cycle gas, after replacement of the ethylene and oxygen transformed. Vinyl acetate was obtained in a yield of 92 %, based on the 8.1 % ethylene conversion rate. This corresponded to a catalyst activity of 495 grams vinyl acetate per liter of catalyst per hour, or to a vinyl acetate yield of 83.2 grams/hr per gram noble metal (Pd + Au). The condensate was found to contain 26.6 weight percent vinyl acetate, and the acetic acid conversion rate was 22.8 %, under these conditions.

EXAMPLE 2:

1350 grams (= 3 liters) of a silicic acid carrier with a particle size between 0.1 and 0.2 mm were mixed and thoroughly kneaded with a solution containing 21.95 grams noble metal ions, namely 16.1 grams Pd⁺⁺ in the form of PdCl₂ and 5.85 grams Au⁺⁺⁺ in the form of H(AuCl₄). The solution contained a quantity of water just sufficient to permit absorption thereof by the silicic acid carrier. The mixture was then dried at about 80°C in a glass tower by the injection of nitrogen.

The dry mass was introduced at 40°C into a 5 % aqueous hydrazine hydrate solution rendered alkaline by means of NaOH or KOH. Following the complete reduction of the noble metal compounds to obtain the corresponding noble metals, the catalyst mass was suction-filtered in a large suction filter under nitrogen, thoroughly washed with water, and kneaded with a concentrated solution of 110 grams potassium acetate in water. The mass was dried at 40-60°C under vacuum and was then ready for use. It contained per liter 7.32 grams noble metals or about 1 weight percent Pd, 0.4 weight percent Au and 3 weight percent K in the form of CH₃COOK.

2.5 liters of the catalyst so produced were placed in a fluidized bed reactor. The reactor was a steam-heated, stainless steel tube (V.A-steel) 3 meters long and 50 mm wide. A tube 125 mm wide was mounted on the reaction tube so as to avoid catalyst losses occasioned by escaping dust. The reaction temperature was controlled using thermocouple elements.

10.3 normal cubic meters/hr of a gas composed of:

- 64 % by volume C₂H₄,
- 16 % by volume CH₃COOH
- 8 % by volume O₂,
- 12 % by volume CO₂.

were passed at 188°C and under a pressure of 8 atmospheres absolute over the

2.5 liters catalyst.

The flow velocity of the gas mixture was 34 cm/second, the contact time was 4.1 seconds, based on the apparent volume (2.5 liters) of the catalyst, and the gas load was 4.12 normal cubic meters per liter of catalyst per hour.

The reaction products were removed from the reaction gas in conventional manner. 600 grams/hr condensate composed of:

- 42.8 weight percent vinyl acetate
- 11 weight percent water and
- 46.2 weight percent acetic acid

were obtained. The catalyst activity was 1026 grams vinyl acetate per liter of catalyst per hour, or 140 grams/hr vinyl acetate per gram noble metal (Pd + Au). Vinyl acetate was obtained in a yield of 90 %, based on the 11 % ethylene conversion rate. The acetic acid conversion rate was 41 %.

Needless to say small proportions of the carrier may consist of particles with a diameter outside the limits of 0.1 to 1.5 mm specified above. It is sufficient for the carrier to be used in a proportion of at least 80 %, for example 85 %, in the form of particles within these limits, without departing from the scope of the present invention.

We draw attention to our Application No. 46567/69, (Serial No. 1266624) which describes and claims the manufacture of (inter alia) vinyl acetate by the use of a carrier catalyst comprising a carrier and one or more palladium compounds.

WHAT WE CLAIM IS:—

1. A process for the manufacture of vinyl acetate by reacting ethylene, acetic acid and molecular oxygen in the gas phase, if desired in the presence of one or more inert gases, at temperatures between 100 and 250°C, under pressures between 1 and 21 atmospheres absolute, and in contact with a carrier catalyst comprising metallic palladium and a carrier, which process comprises carrying out the reaction in contact with a carrier catalyst of which at least 80% of the carrier particles have a diameter between 0.1 and 1.5 mm.

2. A process as claimed in claim 1, wherein the said temperatures are between 150 and 220°C.

3. A process as claimed in claim 1 or 2, wherein the said pressures are between 5 and 11 atmospheres absolute.

4. A process as claimed in claim 1, 2 or 3, wherein the carrier catalyst employed contains additionally one or more of the following activators: the acetates and other carboxylates of lithium, sodium, 130

- potassium, rubidium and cesium, and of magnesium, calcium and the other alkaline earth metals; and the metals copper, gold, zinc, cadmium, tin, lead, manganese, chromium, molybdenum, tungsten, uranium, iron, cobalt, nickel, niobium, vanadium and tantalum.
5. A process as claimed in claim 1, 2, 3 or 4, wherein at least 80% of the carrier particles of the carrier catalyst employed have a diameter between 0.1 and 0.5 mm.
6. A process as claimed in any one of claims 1 to 5, wherein the carrier is silicic acid, preferably globular or ball-shaped silicic acid.
7. A process as claimed in any one of

claims 1 to 6, wherein the reaction is carried out in a fluidized bed.

8. A process for the manufacture of vinyl acetate conducted substantially as described in Example 2 herein.

9. Vinyl acetate whenever obtained by a process as claimed in any one of claims 1 to 8.

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